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6. AUTHOR(S) Richard N. Zare			AFOSR-TR-96 0556	
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13. ABSTRACT (Maximum 200 words) Our research goal was to develop nonintrusive, laser-based optical diagnostic tools for the investigation of trace amounts of molecular species in hostile environments such as plasmas, flashes, flames and other combustion forms. By extending our study on spectroscopic applications of degenerate four-wave mixing (DFWM), we proposed to exploit a new absorption technique, Cavity Ring-Down Spectroscopy (CRDS), which is, in many ways, complementary to other methods for the investigation of the transient species, radicals, and ions present in harsh luminous environments. A spatial profile of CH ₃ absolute concentration near the hot filament was determined by CRDS using a topological method - Abel inversion of the spatial profile of CH ₃ absorbance. No rotational lines are resolved from CH ₃ because of predissociation. A two-photon laser-induced fluorescence (LIF) scheme is proposed to measure atomic hydrogen. The spatial temperature profile near the filament at 20 Torr of pure H ₂ at different filament temperatures was measured in the same reactor we measured CH ₃ . This measurement, combined with the CH ₃ spatial profile gives a better understanding of the two most important gas phase radical species in the hot-filament diamond CVD process.				
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Objective of Research

Our research is in the detection and characterization of molecular and atomic species in highly luminous and hostile environments such as plasmas and flames. We use a variety of optical techniques including degenerate four-wave mixing (DFWM), cavity ring-down spectroscopy (CRDS), and two-photon laser-induced fluorescence (LIF) to look at different species. We are working towards a better understanding of the chemistry in these hostile environments by determining temperature, spatial concentration distribution, and internal state populations of the species under study.

Results of Research

During this past grant period, we continued our exploration into different optical diagnostic techniques for detecting molecular and atomic species in hostile environments. The first studies were conducted with acetylene (C_2H_2) and methyl radical (CH_3) molecules by DFWM in both an atmospheric pressure flame and in a low-pressure hot-filament reactor, in collaboration with Professor C. Kruger, Department of Mechanical Engineering, Stanford University. The next studies, using CRDS, were with CH_3 in a hot-filament reactor of the type used for the growth of diamond films by chemical vapor deposition (CVD). The need for investigation of other species present in the reactor led to studies on measuring atomic hydrogen (H) using two-photon LIF. The details and results of these experiments are discussed on the following page.

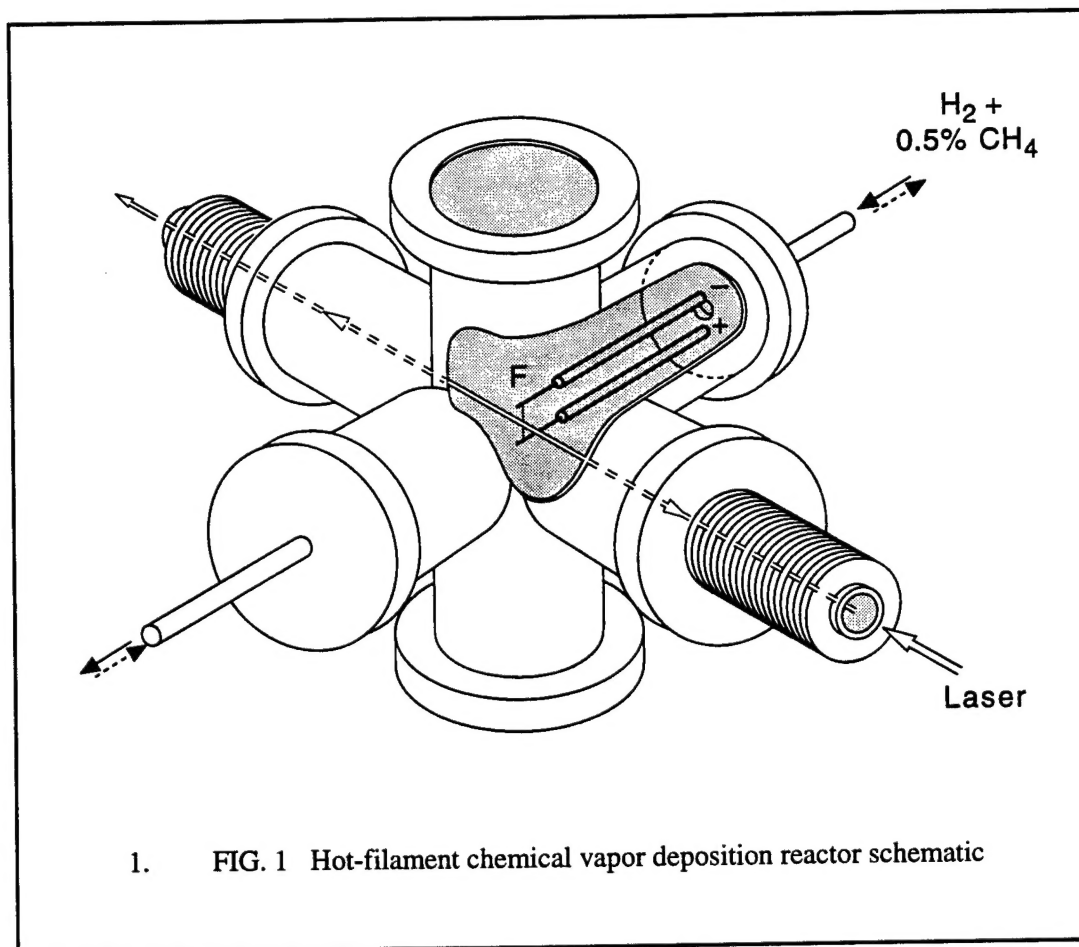
Degenerate four-wave mixing is a nonlinear spectroscopic technique that offers a means of measuring spatially resolved temperature and concentration with a high spectral and temporal resolution. The coherent, phase-conjugate nature of DFWM makes it well suited for probing highly luminous environments. The technique was first tested in an oxy-acetylene flame and explored theoretically for polarization and collision effects. We applied it very successfully to measure the spatial temperature and concentration profile of CH and C₂ in the boundary layer of the inductively coupled atmospheric plasma torch¹. DFWM failed, however, to detect methyl radical (CH₃), the major precursor in diamond growth, because of the predissociation of CH₃ in its first excited electronic state (β_1 -X band at 216 nm). This failure encouraged us to consider absorption measurements that are unaffected by relaxation or predissociation of the excited state.

Cavity Ring-Down Spectroscopy (CRDS) is a linear absorption spectroscopy with high sensitivity, comparable to photo-acoustic spectroscopy. Because the decay of a single pulse stored in a high finesse optical cavity is measured, CRDS overcomes the usual drawback of absorption measurements that suffer from light source intensity variations. A CRDS setup has been designed to measure trace radical species generated in a hot-filament reactor for diamond deposition, and the *in situ* measurement of methyl radical has been successfully carried out under various conditions². A profile of CH₃ absolute concentration near the hot filament has been determined by CRDS using a topological method - Abel inversion of the spatial profile of CH₃ absorbance³. No rotational lines are resolved from CH₃ because of predissociation. Future CRDS measurements of CH radical are expected to resolve rotational lines to obtain a spatial temperature profile as well as the CH concentration.

We chose the hot-filament chemical vapor deposition (HFCVD) reactor because more measurements and computer modeling have been done for this kind of reactor than any other diamond deposition technique. FIG. 1 presents a schematic diagram of the hot-filament reactor used in these measurements². The vacuum chamber consists of a 5-way stainless steel cross 4 inches in diameter. A two-stage mechanical pump (E2M40, Edwards) is used to evacuate the chamber to the minimum pressure of 4×10^{-3} Torr. The chamber is filled with a 20 Torr mixture of H₂ with 0.6 % of CH₄ flowing at a rate of 100 sccm. The tungsten filament is 25 mm long and 0.2 mm in diameter. It is positioned vertically inside the chamber using two tungsten posts, 4 cm long and 1.5 mm in diameter, mounted on water-cooled copper electrodes. The filament is resistively heated with dc current to a brightness temperature of 2400 K, which is monitored with a disappearance pyrometer^{3,4}.

For accurate absorbance measurements, the condition for Beer's law of absorption must be met, which implies that the absorption feature must be wider than the linewidth of the light inside the cavity⁵. This condition is well fulfilled for the methyl radical absorption feature near 216 nm, which is a few nm wide. It is also important that the ground-state population of the absorber molecule is not significantly depleted by excitation during the time the laser pulse is circulating inside the optical cavity. In our experiment, for a 216 nm light pulse of energy about 0.2 μ J and TEM₀₀ mode radius $w = 250 \mu$ m, for mirrors with a reflectivity of $R = 0.991$ and an

effective transmittivity $T_{\text{eff}} \cong 0.003$, and for a CH_3 absorption cross-section $\sigma < 10^{-17} \text{ cm}^2 / \text{molecule}$ ^{6,7}, the fraction of molecules excited by the laser pulse inside the cavity is less than 3×10^{-3} , which is sufficient for accurate CRDS measurements.

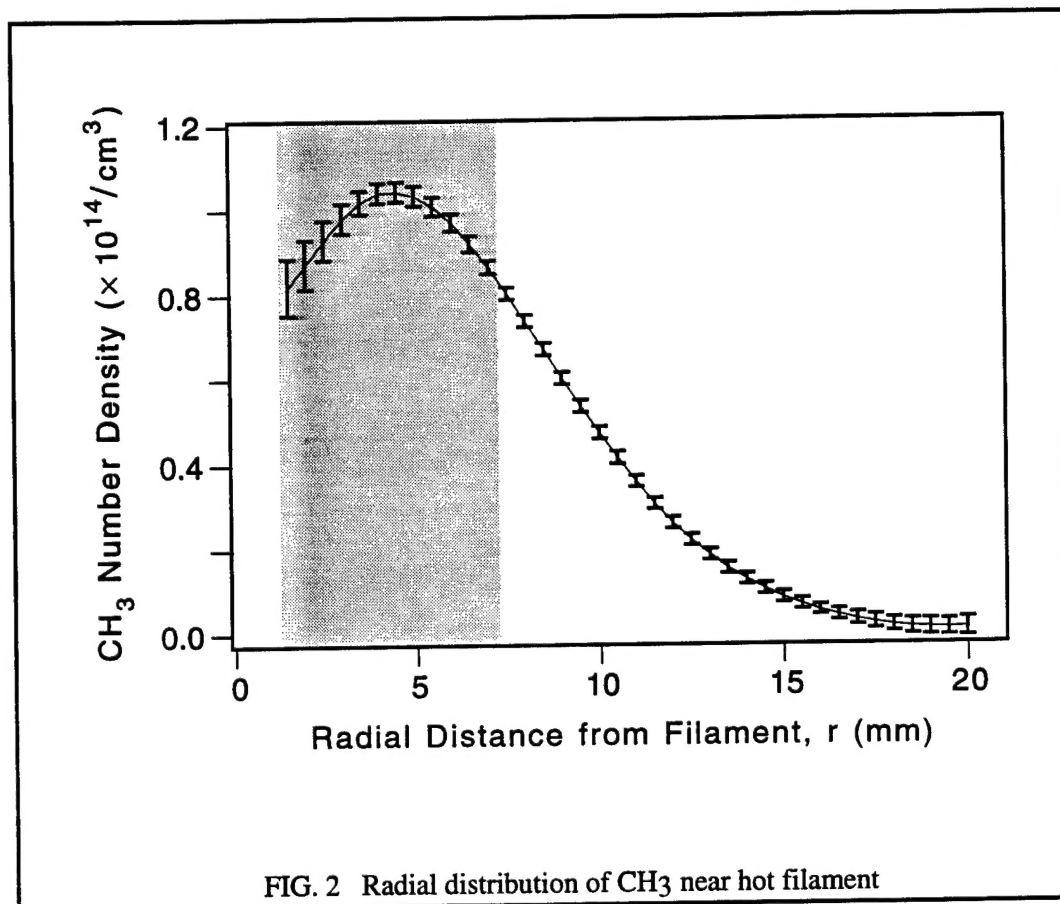


The Abel inversion procedure can be used to convert the absorbance $A(y)$ to the product of the CH_3 number density $n(r)$ times the absorption cross-section $\sigma(r)$:

$$n(r)\sigma(r) = \pi^{-1} \int_r^R (dA / dy) (y^2 - r^2)^{-1/2} dy,$$

where r denotes radial distance from the filament and $A(y)$ vanishes within radius $R = 21.5 \text{ mm}$. The CH_3 absorption cross-section σ at 213.9 nm has been measured and σ was found to be constant within the range of gas temperatures between 1250 K and 2000 K ⁷. Applying the Abel inversion to the profile $A(y)$, and assuming a constant value of $\sigma(r) = 3.98 \times 10^{-18} \text{ cm}^2 / \text{molecule}$, we obtain the radial distribution of CH_3 concentration $n(r)$ presented in FIG. 2.

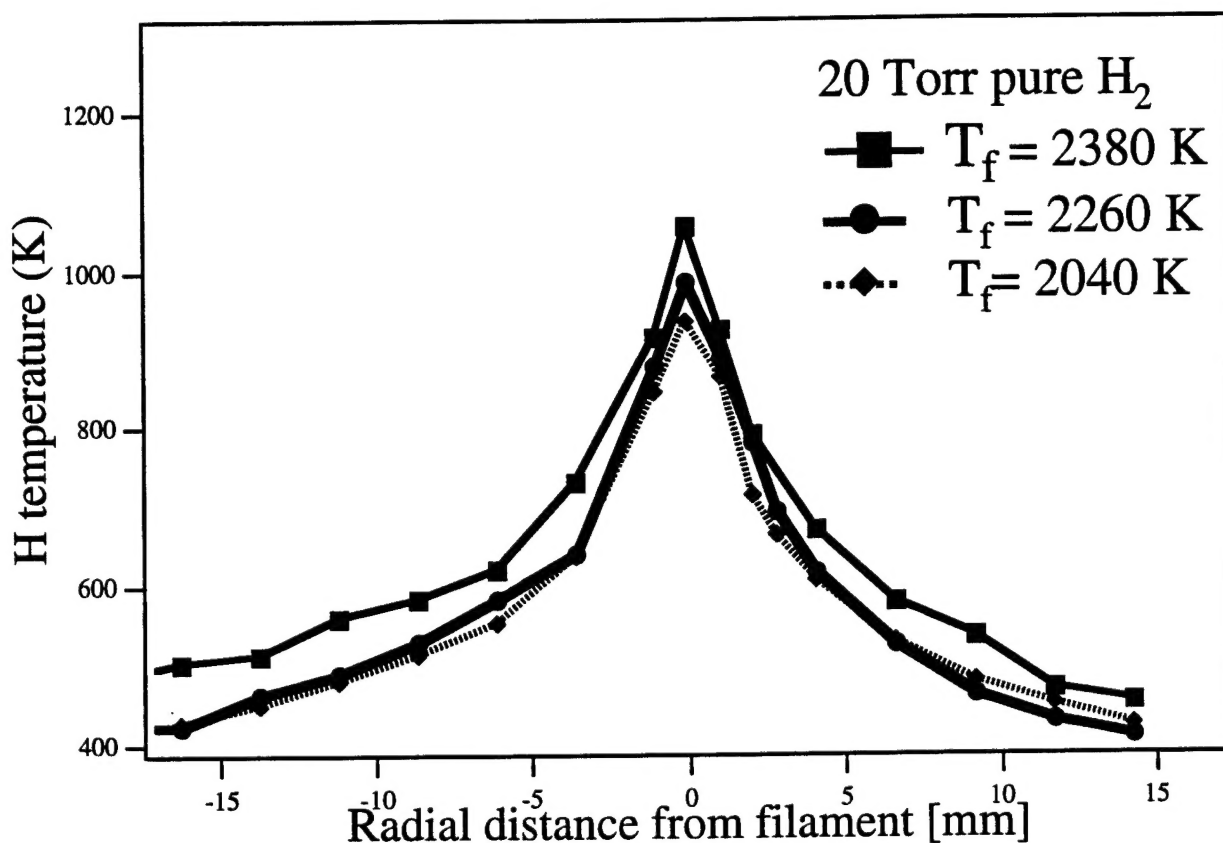
We use the Abel inversion code written by Laux⁸ which inverts a polynomial fit to the experimental data. This approach allows us to estimate the uncertainty in the inverted profile. The error bars represent one standard deviation. The shaded part of the figure indicates radial distances from the filament where the gas temperature is between 1250 K and 2000 K³. Based on a hydrogen diffusion model, methyl concentration should peak at the filament. However, it was unexpectedly observed to peak about 5 mm from the filament. This behavior is possibly the result of the Soret effect or the dissociation of methyl near the filament.



This research also includes determination of the conditions under which CRDS can be used for quantitative measurement of absolute concentrations of molecular species⁵. The conditions useful for CRDS diagnostics have been estimated by analyzing how the absorption loss measured by CRDS varies with the sample absorbance for various ratios of the laser pulse linewidth to the absorption linewidth. A wide range of conditions was found in which the sample absorbance (and consequently absolute number density) can be recovered from the CRDS spectrum. We therefore expect CRDS to find a broad range of applications in combustion studies, materials processing, and atmospheric chemistry investigations. However, this new spectroscopy needs additional work, in both theory and application, before it can be applied with confidence and success to different conditions. Theoretical investigations on the influence of

interference effects (etalon) on spectroscopic studies and the influence of various mode-beating effects are being carried out in our laboratory; experimentally, we are proposing to study other possibilities of improving CRDS performance, such as data acquisition techniques other than an oscilloscope, and more cost-effective light sources, like diode lasers and other CW laser sources chopped with a mechanical or acousto-optic modulator. Our new Optical Parametric Oscillator (OPO) laser system will extend our CRDS ability from the UV/VIS to the IR in order to explore the 3 μm "fingerprint" region of many hydrocarbon free radicals (CH_3 , CH_2 , CH , C_2H , etc.) that exist under plasma diamond deposition conditions.

Atomic hydrogen (H) plays an important role in the diamond CVD synthesis environment by affecting the quality and quantity of diamond films produced. Because of the large energy spacing between the H ground state 1s to its first excited 2p state (10.2 eV), single-photon optical techniques would require generation of 121.5 nm in the vacuum ultraviolet. We are developing



an alternative approach involving a two-photon LIF experiment to determine both the temperature and concentration in a hot-filament reactor. In this technique, a ground-state hydrogen atom excited from 1s to 2s by absorbing two photons of wavelength 243 nm, is collisionally mixed with 2p and fluoresces to the 1s level. Lyman- α emission at 121.5 nm is detected and the H temperature is measured from the Doppler line width of the two-photon absorption with the linewidth of 1.12 cm^{-1} at 1500 K. A solar blind photomultiplier tube with a

narrow bandpass filter centered at Lyman- α in front is directly sealed to the reactor to detect photons at 121.6 nm. Due to the low saturation current (1-10 nA) of the PMT, attention must be paid to maintain the supply voltage low enough to retain the linear response of the PMT. The cesium iodide photocathode threshold at approximately 220 nm rendered the long wavelength rejection that significantly reduces the incandescence background of the hot filament. The quiet background results in two major advantages in comparison with most other two photon LIF schemes of H detection by monitoring the Balmer series. First, the high detection sensitivity requires less amount of H density to achieve a good lineshape measurement; secondly, the temperature derived from the Doppler linewidth has a much high precision, in average standard deviation less than 50 K, over a wide dynamic range of gas phase temperatures, from 400 K to 2000 K or higher. FIG. 4 shows the spatial temperature profile near the filament at 20 Torr of pure H_2 at three different filament temperatures in the same reactor in which we measured CH_3 .⁹ This measurement combined, with the CH_3 spatial profile, will give a good picture of the two most important gas phase radical species in the hot-filament diamond CVD process.

From the resonance reabsorption of Lyman- α fluorescence, the absolute H concentration can be derived without the need for additional calibration under the geometry of a cylindrical H distribution around the filament of the hot-wire reactor. In general, the LIF signal is linearly proportional to the concentration of the fluorescence species and gives the relative concentration or even absolute concentration after additional calibration with a sample of known concentration. However, resonance radiation causes difficulty in extracting from the post reabsorption LIF signal the relative concentration of H atoms because quantitative evaluation of the reabsorption requires the distribution of the fluorescence species being measured. Lyman- α emission is resonance radiation because it is an optical transition from an excited state to the ground state, and the large population of the ground state causes significant reabsorption (self-absorption) of the emitted light [resonance radiation has been well described by Holstein's equation]¹⁰⁻¹². We have a relatively thin optical medium so that Lyman- α emission is not completely imprisoned by the surrounding atomic hydrogen, because the Doppler effect lowers the total effective absorption cross section, and in the HFCVD reactor, the hydrogen concentration is on the order of 10^{14} atom / cm^3 ^{13,14}. Therefore, from the resonance reabsorption of Lyman- α fluorescence, under the geometry of cylindrical H distribution around the filament, the absolute H concentration can be derived without the need for additional calibration [assuming H_2 absorbs Lyman- α radiation to a negligible extent]. Although numerous methods exist for determining the temperature, our proposed method has the special advantage of measuring both the temperature and the concentration. Moreover, the concentration can be determined on an absolute basis. This last measurement is of particular value because most other methods only yield the relative concentration. The precision and reliability of the concentration still needs to be calibrated or confirmed as the future investigation.

References

1. D. S. Green, T. G. Owano, S. Williams, D. G. Goodwin, R. N. Zare, and C. H. Kruger, *Science* **259**, 1726 (1993).
2. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, and C. H. Kruger, *Chem. Phys. Lett.* **234**, 269 (1995).
3. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, T. G. Owano, and C. H. Kruger, *Appl. Phys. Lett.* **67**, 144 (1995).
4. P. Zalicki, Y. Ma, R. N. Zare, J. R. Dadamio, E. H. Wahl, T. G. Owano, and C. H. Kruger, in *Proceedings of 47th Annual Gaseous Electronics Conference*, Gaithersburg, Maryland USA, 1994, edited by city, year published), p.
5. P. Zalicki and R. N. Zare, *J. Chem. Phys.* **102**, 2708 (1995).
6. W. C. J. Gardiner, S. M. Hwang, and M. J. Rabinowitz, *Energy & Fuels* **1**, 545 (1987).
7. S. M. Hwang, M. J. Rabinowitz, and W. C. G. Jr., *Chem. Phys. Lett.* **205**, 157 (1993).
8. C. O. Laux, Ph.D. Thesis, HTGL Report T-288, Mech. Eng. Dept., Stanford University, 1993.
9. Y. Ma, P. Zalicki, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, and C. H. Kruger, Gordon research conference on diamond synthesis, New Hampshire (1996).
10. T. Holstein, *Phys. Rev.* **72**, 1212 (1947).
11. T. Holstein, *Phys. Rev.* **83**, 1159 (1951).
12. R. Lai, S. Liu, and X. Ma, *Z. Phys. D* **27**, 223 (1993).
13. S. J. Harris and A. M. Weiner, *J. Appl. Phys.* **67**, 6520 (1990).
14. S. J. Harris and A. M. Weiner, *J. Appl. Phys.* **74**, 1022 (1993).